REVISION 2

The rapid expansion of environmental mineralogy in unconventional ways: Beyond the accepted definition of a mineral, the latest technology, and using nature as our guide

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ABSTRACT

Environmental mineralogy is rapidly expanding in technological directions that allow for the detection, characterization, and understanding of non-crystalline and poorly crystalline phases, crystalline-amorphous mixed phases, and nanosized naturally-occurring materials. Specifically, this article provides a perspective view of the broad range of structural complexity/heterogeneity observed in environmental minerals and amorphous materials, as well as our current understanding of how these materials can be best observed, evaluated, and described, and why this is important in the mineralogical sciences. The discussion is broken down into the assessment of short- and medium-range order in amorphous materials, and the nature of nanominerals and mineral nanoparticles, amorphous-nanocrystalline transitional phases, and mesocrystals. These materials do not fit one or more aspects of the most commonly used definitions of a mineral (although some of them are formally recognized as minerals, such as ferrihydrite and schwertmannite), yet they do fit other portions of these current definitions. Nevertheless, because these phases can be exceptionally minute in size, and/or not highly crystalline, and/or generally much less abundant than other mineral components in the system, they may be underappreciated and/or understudied, or, apparently as is often the case, completely missed. Yet they are often highly relevant to, and in many cases dominant in, important aspects of how the (bio)geochemistry of an environmental system operates. Further, although it is important to analytically and experimentally characterize synthetic equivalent phases in the laboratory, often under conditions intended to mimic one or a few aspects of the real environment, we argue that it is imperative to study natural, intact (as much as possible) samples and make field measurements with much greater frequency than is currently practiced.

KEYWORDS

Environmental mineralogy, synchrotron radiation, free electron laser, transmission electron microscopy, nanomineral, mineral nanoparticle, polyphasic nanomineral, prenucleation cluster, non-classical crystallization, mesocrystal.

INTRODUCTION

It is very well known, especially among mineralogists, geochemists, and geophysicists, that knowledge of atomic structure has proven crucial time and again in understanding mineral behavior including: compressibility, elasticity, thermal behavior, density, hardness, optical properties, solubility, adsorption and desorption tendencies, transformation characteristics, thermodynamic properties, etc. Indeed, the accessibility of such information through mineralogy has had tremendous implications for our understanding of geological and environmental processes on Earth as well as on other planets.

Yet despite the obvious importance of atomic structure and the central role that it plays, it has become more apparent over the years that crystallinity is the most difficult aspect to measure and describe, especially when the periodicity of the structure is reduced. Further, as we point to throughout this paper, this can be viewed as having fundamental consequences in terms of being able to express a precise definition of a mineral. A classic and still widely-accepted definition of a mineral can be stated as follows: a solid formed as a result of a geological process and characterized by a periodic array of atoms with a known structure, definite chemical composition, and discrete (indexable) diffraction signature (Nickel 1995; International Union of Crystallography, Report of the Executive Committee for 1991). Nevertheless, especially over the last 20 years, the reported definitions of a mineral, as stated in introductory geoscience- and mineralogy-related textbooks and on-line, generally have become progressively broader and more detailed. To some extent, this is likely due to advancement of the mineralogical sciences that is, in part, driven by new characterization tools and methods, and also by an expansion of the types of scientists who are interested in minerals. Recently, French et al. (2012) compiled up-to-date, authoritative descriptions of the term mineral, producing the following definition: “Currently, minerals are most commonly defined as naturally occurring substances, produced by (bio)geochemical processes, with a highly ordered, repeating atomic arrangement (a crystalline substance) whose composition can be described by a chemical formula that is either fixed or variable (or, also as often stated, a definite, but not necessarily fixed, composition). Samples of the same mineral vary in terms of minor and/or trace element composition, and in the case of solid solution, major element composition, as long as these substitutions do not change the average crystal structure. Finally, it follows that minerals of the same major and minor

element composition will express a set of measureable and consistent physical and chemical properties." Even this definition can be reasonably challenged and/or debated in various places (e.g., among many others, Klein and Dutrow, 2008; Hochella et al., 2008; Bindi et al., 2011; Bindi and Steinhardt, 2012; French et al., 2012).

Whatever the exact definition of mineral that one uses, such descriptive elements are broadly applicable to what we observe in vast assemblages of fundamental Earth materials that comprise the igneous, sedimentary, and metamorphic rocks in Earth's crust, as well as the thin veneer (relatively speaking) of soil and aqueous environments encompassing Earth's near-surface. In this regard, crystallinity has always been quintessential in terms of what defines a mineral because three-dimensional periodicity (except in quasicrystals) is what makes the average atomic structure accessible by modern diffraction methods. The Rietveld method (Rietveld, 1969) of analyzing single crystal and powder diffraction data in reciprocal-space has long been the standard for determining long-range structure in crystalline materials. Indeed, modern Bragg diffraction and crystallographic methods have revealed the average crystal structures of several thousand minerals to date, not to mention several hundred thousand organic, organo-metallic, and inorganic compounds, and metals and alloys that are not naturally-occurring.

Although crystallinity is abundant in Earth materials, it is important to bear in mind that crystals produced in nature (and laboratory) are not flawless at the atomic level. Local atomic displacements away from the average long-range structure are present even in the most highly crystalline materials due to occurrences of point (e.g., vacancies or substitutions of atoms), linear (dislocations), and planar (grain boundaries, stacking faults, external surfaces) defects. Imperfections in gem-quality natural diamonds, for example, often are the result of vacancies, dislocations, and atomic inclusions of impurities e.g., nitrogen or boron. In the case of diamond, as well as for numerous other minerals, defects and lattice relaxation around the defects (e.g., strain) are extremely important due to the considerable impacts they have on optical, physical, chemical, or mechanical properties. In addition to internal structural defects in crystals, we also now know that the arrangements of atoms at and near the surfaces can differ substantially from their bulk equilibrium positions, and normally are not fully represented by models based on ideal surface terminations of the bulk structure. The phenomenon of surface relaxation and reconstruction, which includes modifications in periodicity, symmetry changes, and an overall increase in structural disorder in the first few atomic layers near the surface of the crystal, is inevitable as the system strives to reduce

surface free energy. These changes in crystal structure at the mineral-water (and mineral-air) interface are extremely important and can be tied directly to mineral chemical behavior (e.g., Trainor et al., 2004). Whether occurring primarily at the surface or in the bulk, it is clear that structural disorder restricts perfect periodicity to varying degrees in *all* natural crystals, yet we still classify them as minerals because they fit the consensus definitions in being "highly ordered" or having a "known structure". This is usually not the case for much of nature's solids that are exceptionally minute in size (i.e., nanosized), and/or not highly crystalline.

Indeed, if no natural crystal is perfect and disorder is always part of atomic structure, the question arises: How much disorder is acceptable in the classification of a mineral? The point of this *Outlook* article is not to attempt to answer this question, which most would agree exists on a slippery slope, but to make the point that environmental mineralogy has been rapidly expanding in the direction of the detection, characterization, and understanding of poorly crystalline, partially amorphous, and/or nanosized naturally-occurring materials that do not fit one or more aspects of the most commonly used definitions of a mineral (mainly in the areas of crystallinity and homogeneity); yet they do fit other aspects of the definition well. Indeed, relatively recently, very poorly ordered as well as partially amorphous environmentally important substances, such as ferrihydrite and schwertmannite, have been formally recognized as minerals. Perhaps these have been recognized as official minerals not only because of their widespread abundance and/or critical geochemical importance, but because when they were recognized as "minerals", their detailed nature was not fully realized or appreciated. In the meantime, our understanding of the structures of these materials, including the nature of structural order and disorder, has markedly improved due to the advancement and development of a suite of atomic structure analysis tools, including computational methods.

Addressing these issues, the current article presents a perspective view of the wide range of crystallinity and structural complexity/heterogeneity observed in environmental systems, how these structures can be best observed, evaluated, and described, and why it is such an important emerging research area especially within the field of environmental mineralogy.

WHEN TECHNOLOGY LIGHTS THE WAY

The study of mineral crystallinity has always been limited by our technical ability to infer the arrangement of atoms in a crystalline structure. Without any doubt, the discovery of

X-rays in 1895 by Wilhelm Conrad Röntgen and its later application to the study of mineral crystal structures, by means of the X-ray diffraction phenomena and Bragg's law (Bragg, 1912), has been the most important technical revolution in this field. Since then, some other very important techniques have been incorporated into the study of mineral crystallinity such as electron and neutron diffraction, nuclear magnetic resonance (NMR), and infrared and Raman spectroscopy, among others (Fig. 1A). Although not suitable for determining structure directly, it is also noteworthy that optical mineralogical methods and use of the polarizing light microscope has contributed immensely to our knowledge of minerals and rocks.

However, a second technological revolution, during the last 20 years, is launching the fields of mineral crystallinity and environmental mineralogy to an entirely new dimension. This new era mainly relies on the discoveries and innovations achieved in both synchrotron light sources and transmission electron microscopy (TEM).

Synchrotrons generate intense radiation (from the infrared to 'hard' X-rays in the electromagnetic spectrum, Fig.1 B) and typically display high brilliance, tunability, low divergence and low emittance of the beam. The first dedicated parasitic synchrotron light sources were developed in the mid-1970s. Since that time, new generations of synchrotrons have progressively become optimized for high brilliance (or brightness). Peak brilliance (PB = photon flux per unit transverse and longitudinal phase-space volume, photons/sec mrad^2 mm^2 0.1%BW) in the current "3rd generation" synchrotron radiation facilities has increased more than nine orders of magnitude (10^{19} to 10^{25} PB, Fig. 1B) compared to conventional X-ray sealed tubes (10^8 to 10^{10} PB), allowing the appearance or enhancement of a variety of X-ray techniques. In general, this is because cyclic accelerators are uniquely equipped with insertion devices that alter the properties of the X-ray beam. These devices typically include wigglers, which provide continuous energy spectrums, and undulators, which operate at discrete energies but deliver extremely high flux. Other devices used for conditioning the characteristics (specific energy, dimensions, etc.) of the radiation beam include monochromators, mirror optics, collimators and slits, among others. These elements are typically combined with state-of-the art 1-D and 2-D detector systems having high spatial and/or energy resolution that measure the radiation that has interacted with the sample. Overall, synchrotron beamlines are typically equipped for spectroscopy, scattering, and/or imaging experiments and the facilities are designed to accommodate a broad range of studies involving chemistry, physics, biology, and materials sciences.

Modern synchrotrons support a wide variety of methods and experiments that are well suited for the earth sciences, including studies of mineral crystal chemistry and mineral behavior in complex earth material matrices. The unique properties of synchrotron light, in particular the brightness and tunability, has permitted the growth of many X-ray scattering based techniques such as X-ray total scattering and pair distribution function (PDF), small angle X-ray scattering (SAXS), surface X-ray scattering methods such as crystal truncation rod (CRT) diffraction, photoelectron scattering (X-ray absorption fine structure, XAFS), and grazing incidence methods (e.g., long-period X-ray standing wave, LP-XSW). Synchrotron light has also enhanced some well established techniques (e.g., μ-XRD and μ-XRF) which have gained spatial resolutions down to 100 nm. These methods open up the possibility of studying characteristics of minerals with sensitivities and at resolutions that are normally not achievable with laboratory X-ray sources. Static experiments of single crystal and polycrystalline samples at ambient conditions are common, and include studies of bulk structures and the nature of defects and disorder in natural materials ranging from crystalline to amorphous. In addition, many of the aforementioned techniques allow studies of minerals in situ under a wide variety of conditions ranging from water at environmental conditions (Majzlan and Myneni, 2005) to melts or solids at high P-T conditions (e.g., 73GPa and 1700K; Lin et al., 2005). For additional information on synchrotrons and the use of synchrotron radiation in the study of Earth materials, the reader is referred to the *Elements* issue entitled "User research facilities in the Earth Sciences" (Sutton, 2006) and articles therein.

Although the trend of increasing brightness in synchrotrons over the last 30 years has been impressive, the limits are now being pushed even further by the new generation of free-electron lasers (FEL) that, just in the last five years, have been able to achieve peak brilliances (10^{29} to 10^{34} PB) nine orders of magnitude higher than the current 3rd generation synchrotrons (Fig. 1B). In addition to this outstanding peak brilliance, FELs typically display ultrashort pulse durations of about 100fs (at least 100 times shorter than common synchrotrons), and 7fs pulses have been demonstrated using the Linac Coherent Light Source (LCLS) at Stanford University, USA. These unprecedented conditions are paving the way to explore new fields in mineralogy like femtosecond nanocrystallography and coherent X-ray imaging with nanometer resolution as recently demonstrated with a pioneering study of soot particles in flight (Loh et al., 2012). For additional information and perspectives in FELs, the reader is referred to Ullrich et al. (2012).

Transmission electron microscopy is the other essential pillar supporting many of the new discoveries in mineral crystallinity and environmental mineralogy. Since the first TEM was built by Max Knoll and Ernst Ruska in 1931, imaging resolution has improved by nearly three orders of magnitude, starting at roughly 10 nm (Fig. 1C) for the first commercial instruments in the late 1930's (Rickerby et al., 1999), to atomic resolution (0.045 nm) achieved by the current aberration-corrected high resolution-TEMs (Barton et al., 2012). In addition to atomic scale imaging, the interactions between an electron beam and the constituent atoms of a sample also generate a wealth of information that can be interpreted by the use of various powerful analytical techniques such as electron diffraction (ED; often essential for phase identification, but also used for a wide variety of crystallographic studies) and selected area electron diffraction (SAED; ED from areas ranging from microns to 5-10 nanometers in diameter); energy-dispersive X-ray spectroscopy (EDS; chemical analysis with spatial resolution down to single atomic columns, now using exceptionally efficient large area silicon drift detectors); energy filtered TEM (EFTEM, imaging formed from electrons of a particular energy only); electron energy loss spectroscopy, especially when combined with EFTEM imaging (EELS); electronic structure and bonding studies; electron tomography (3-D images of any object in a TEM specimen); high angle annular dark field scanning TEM (HAADF-STEM; image contrast as a result of average atomic number at every position of the highly focused scanning beam, and also used for tomographic images); and high resolution TEM (HR-TEM; lattice fringe imaging, with corresponding fast Fourier transform – FFT – images). All of these imaging, analytic, and crystallographic capabilities place electron microscopy as possibly the single most versatile technique in mineralogy today.

These exceptional advances in electron microscopy are leading to new studies almost unthinkable just a decade ago, such as highly detailed three dimensional imaging of nanoparticles, and dynamic observations of the physical behavior of nanoparticles in aqueous solutions. Concerning the former, some of the unique attributes of nanominerals arise from three-dimensional (3D) spatial features. In principle, electron tomographic reconstructions use algorithms to infer 3D geometry from a series of conventional 2D projections taken from different perspectives. It has been shown recently that 3D reconstructions give more accurate nanoparticle size and spacing information than conventional 2D imaging (Monsegue et al., in press). At atomic resolution, it is much more challenging to achieve electron tomographic reconstructions because the 2D micrographs must be aligned with a spatial accuracy better

than the imaged interatomic spacing. Nevertheless, several electron tomography strategies have been developed to achieve reconstructions with full atomic-scale resolution (Van Aert et al., 2011; Van Dyck et al., 2012; Scott et al., 2012). There are practical challenges to implementing these strategies, however, including difficulty tilting a sample through large angles with enough mechanical precision to permit atomic resolution reconstruction, and the need to rely on an assumed structure model to infer atom positions along the electron beam direction. A model-free strategy was recently demonstrated (Scott et al., 2012), but accurate image alignment remains a barrier to reconstructing arbitrary/defective nanostructured crystals with atomic resolution.

Finally, recent advances in *in situ* TEM offers dynamic observations of the physical and chemical behavior of nanominerals in response to external parameters including temperature, atmosphere, stress, solutions, etc; that may be far from equilibrium conditions (if desired) in relatively short to moderate periods of time (hours to days). After many decades of hardware development, reliable environmental cell construction for examining solid-gas, solid-solid and liquid-solid phase interactions are now commercially available, allowing for imaging at sub-nanometer resolution levels (see, e.g., Woehl et al., 2013). For nanoparticles, particularly important recent advances include the observation of oriented attachment of nanominerals in aqueous solution and in real time (Li et al., 2012), and nanocrystalline growth in aqueous solution viewed with atomic resolution in real time (Yuk et al., 2012). These types of studies show phenomena that have never been observed and/or predicted before, and therefore are revolutionary in advancing science.

Comprehensive information about transmission electron microscopy and associated techniques can be found in the compendium by Williams and Carter (2009).

As shown in Figure 1A, it is worth noting that each of the many analytical techniques available to study mineral crystallinity has a specific “high efficiency” limited range. Consequently, it is essential to realize that the current revolution in the study of mineral crystallinity and environmental mineralogy is, and will be, possible not only because of the advances in a few analytical techniques, but mainly because of the synergistic interaction among the many techniques covering different scales and analytical approaches.

EMERGING AREAS IN THE FIELD OF MINERAL CRYSTALLINITY FOR ENVIRONMENTAL SYSTEMS

For the sake of clarity and to facilitate the discussion in the following sections, the natural progressive transition between amorphous and crystalline materials will be categorized according to material periodicity and size (Fig. 2). Material periodicity can be understood as the nature of regularly appearing recurrent motifs as one moves through an atomic structure, and it is convenient to compartmentalize this regularity in terms of short-, medium- and long-range order. The structure of a crystal is composed of a unit cell that repeats by translational symmetry. As such, long-range order (LRO) is referenced to the translation from one site to another identical site in a different unit cell in a crystal structure. Short-range order (SRO), on the other hand, is referenced to a single atom or point in a structure versus some nearby neighboring atom or shell of atoms. Medium-range order (MRO), a term that is more often used in literature pertaining to glasses and liquids, is simply an extension of SRO (e.g., third, fourth, etc. coordination shells). Figure 2 presents these brief definitions of SRO, MRO, and LRO in terms of interatomic distances. As shown, SRO is typically limited to periodicity that extends to the third nearest atomic neighbor (distances generally on the order of up to 0.5 to 0.6 nm), MRO extends periodicity from the fourth to the tenth nearest neighbor (up to 2 to 3 nm, depending on bond lengths), and finally LRO accounts for periodicity beyond the tenth nearest neighbor (Lucovsky, 1987). In accordance with the possible scientific fields defined by this categorization (Fig. 2), the following emerging areas in material periodicity/crystallinity in environmental systems will be discussed: SRO and MRO in amorphous materials, nanominerals and mineral nanoparticles, amorphous-nanocrystalline transitional phases, and mesocrystals.

Short- and medium-range order in amorphous materials

As in the case of crystalline materials, having the correct structural model of an amorphous solid is important in order to understand its physical-chemical characteristics and behavior in both natural and materials science settings. Characterizing the structures of amorphous materials is challenging, however, due to the absence of the sharp Bragg spots or lines that arise from lattice periodicity (*i.e.*, LRO) in crystalline materials. In materials lacking LRO, methods for evaluating structure, and the models derived from these methods, focus on describing the structural ordering over short- and medium-range length scales. For SRO within compounds, such as a silicate glass, the arrangements of atoms in this region define the coordination polyhedra, as well as the basic connectivity of these units in a

313 structure. MRO describes correlations between pairs of atoms that occur from the linkages
314 between coordination polyhedra at greater distances, which in some amorphous structures
315 can reach a few nanometers (Wright, 1998). Recent studies have shown that our ability to
316 quantify the short- and medium-range structure of amorphous materials continues to improve
317 due to advances in both experimental approaches and in structural analysis using
318 computational methods.

319 The atomic pair distribution function (PDF) technique has been one essential tool in
320 the development of our understanding of structure in solids that range from exclusively short-
321 range ordered (i.e., amorphous/glassy) to crystalline with some disorder, as well as in
322 materials that can be thought of as existing between crystals and glasses (nanocrystalline,
323 nanoscale and poorly crystallized, paracrystalline, polyphasic, etc.). The PDF is the Fourier
324 transform of the scattered intensity and describes the real-space distribution of interatomic
325 distances in a sample. Unlike Bragg diffraction and crystallographic methods that focus on
326 the occurrences of sharp peaks, the PDF approach does not rely on the presence of LRO.
327 This is important since a significant proportion of the total integrated intensity resides in the
328 diffuse scattering in cases of substances that are nanoscale, partially crystallized, and/or
329 completely disordered. Although the diffuse intensity is relatively weak compared with
330 Bragg intensity, and is also widely spread over reciprocal space, it contains important
331 information regarding the SRO and MRO in a sample. A total scattering experiment, from
332 which the PDF is calculated, measures both the Bragg and diffuse scattering and treats these
333 on an equal basis. As a result, the method is capable of revealing average structure in
334 materials that range from crystalline to highly disordered, and virtually everything in
335 between.

336 From the first study by Debye in 1915 (Debye, 1915) up until the mid-1980s, X-rays
337 were routinely used in PDF studies because of the availability of laboratory sources. Work
338 focusing on liquids and amorphous solids during this period resulted in remarkable advances
339 in our understanding of structure in silica glass, liquid water, and liquid mercury, just to
340 name a few (see Billinge, 2004, and articles therein for additional information on early works
341 and the history of PDF). Since the early pioneering works, a great many diffraction studies
342 of amorphous solid (and liquid) samples have been carried out (see Klug and Alexander,
343 1974; Warren, 1990; Wright, 1998). Although PDF studies using laboratory X-ray sources
344 continue, a number of recent studies of amorphous solids have taken advantage of the intense
345 sources of radiation that are available at 3rd generation synchrotron sources. Some of these

have involved studies of natural or synthetic analogues of amorphous solids including carbonates (e.g., Michel et al., 2008, Goodwin et al., 2010; Radha et al., 2012; Reeder et al., 2013), and silicates (e.g., Poulsen et al., 1995). One benefit of synchrotron radiation is that high energies (up to 100 keV) allow access to significantly higher scattering angles (or momentum transfer, Q) than is available for most conventional lab sources (e.g., those equipped with Cu or Mo anode materials). The result is a PDF with higher resolution and lower termination errors, which are artifacts related to the finite range of scattering data that is included in the Fourier transform. The extraordinary brilliance of synchrotron X-rays provides an additional benefit that allows the rapid and accurate measurement of diffuse intensity, which dominates in amorphous materials, but can be up to 8 orders of magnitude less than the Bragg intensity observed for polycrystalline samples.

Comprehensive information about total scattering and PDF analysis methods can be found in Egami and Billinge (2003). It is noteworthy that neutrons are used in place of X-rays in some total scattering/PDF experiments, and can offer distinct advantages depending on the elements involved (Proffen 2006). For additional information on the use of neutron scattering in mineral sciences, the reader is referred to Dove (2002) and articles therein.

Synchrotron X-ray absorption spectroscopy is a technique that has also greatly added to our understanding of local atomic structure in amorphous solids. The origins of XAS date back to the 1920's and 30's (for review see Lytle, 1999). Modern XAS measurements are typically done using synchrotron X-ray sources since they are able to provide a continuous and intense X-ray source covering a broad range of energies. XAS data are obtained by monitoring the interaction of X-rays with a sample as the incident X-ray energy is varied across an absorption edge (e.g., K or L_I, L_{II}, L_{III}, etc.). A sharp change in the transmitted (and fluoresced) signal occurs when the energy of the incident photon corresponds to the energy of a shell of the absorbing atom. The spectral region containing this "white line", which is the intense feature within about 10 eV of this absorption threshold position, and the features within ~50 eV above this threshold, is referred to as the X-ray absorption near edge structure (XANES). XANES data are typically used to obtain information regarding the oxidation state and site symmetry of the absorbing atom. The spectral region extending from ~50 eV to ~1000 eV above the absorption threshold is referred to as the X-ray absorption fine structure (XAFS). XAFS is typically used to obtain structural information such as separations (*e.g.*, bond lengths) and coordination numbers of atom pairs in the structure for the absorbing element. In the case of amorphous materials, the information from XAFS is typically limited

to length scales that are part of the SRO. Further, when used with amorphous or disordered materials, XAFS has the problem of inaccuracy in terms of atom-pair distances and coordination numbers (see Crozier et al., 1988). Nevertheless, XAS methods can provide an ideal complement to bulk structural data based on scattering measurements because they are element-specific and are suitable even when the element of interest is at low concentration (usually down to 10's of ppm) in a sample.

A comprehensive review of XAS methods and applications in mineralogy and geochemistry can be found in Brown et al. (1988) and Henderson et al., (2014).

Finally, recent development of a TEM-based technique known as fluctuation electron microscopy (FEM), which is a hybrid imaging-diffraction method (Treacy et al., 2005), is proving to also be a valuable tool in studying the structures of amorphous materials. FEM can provide specific sensitivity to MRO of an amorphous material and has the advantage of sampling from small sample volumes. Recent FEM studies of amorphous silicon (a-Si) indicate the presence of paracrystalline ordered regions (that is showing SRO and MRO, but not LRO) in the 1 to 2 nm length scale (Treacy and Borisenko, 2012a), a provocative finding (Roorda and Lewis, 2012; Treacy and Borisenko, 2012b) that challenges the widely accepted notion that the structure of a-Si is well represented by the continuous random network (CRN) model. To date, FEM has been applied mainly to materials of technological interest such as amorphous semiconductors, disordered carbons, and metallic glasses (see Borisenko et al. 2012, and references therein). We anticipate that future FEM studies will begin to include structural characterization of amorphous and poorly crystallized components in natural solids collected from environmental systems.

Experimental data derived from these various methods are analyzed via computational approaches that include molecular dynamics (MD), density functional theory (DFT), (reverse) Monte Carlo methods, and empirical potential structure refinement (EPSR), to name just a few.

Nanominerals, mineral nanoparticles and colloids

Natural nanosized particles in environmental systems have been studied for decades and are an important part of the range of environmental colloids (Stumm and Morgan, 1970). In the full colloids category, a myriad of organic, inorganic, and organic/inorganic mixed particles with one or more dimensions in the 1 nm to 1μm size range are covered. However, especially in the last decade, a new field of study restricted to nanoscale minerals and mineral nanoparticles, known as nanomineralogy, is growing apart from the traditional colloidal

412 fields. The foundational characteristic of nanominerals (minerals only existing in the
413 nanoscale) and mineral nanoparticles is to have at least one dimension spanning the range of
414 1 nm to 100 nm; however, it is the often dramatic change in their physical and chemical
415 properties as a function of their size that makes them unique in nature. Among the vast recent
416 literature covering these phenomena, some representative examples are: up to two orders of
417 magnitude faster Mn^{2+} oxidation rates per surface area due to smaller nanoparticulate iron
418 oxide catalysis (comparing 7 nm vs. 37 nm hematite nanocrystals; Madden and Hochella,
419 2005), higher phytotoxicity of ZnO nanoparticles compared with micrometer ZnO particles at
420 equivalent concentrations (Yuwono et al., 2010), titanium dioxide mineral dissolution rates
421 as a function of size (Schmidt and Vogelsberger, 2006),

422 It is worth noting that the recent remarkable increase in the study of nanominerals and
423 mineral nanoparticles is attributed not only to their numerous applications in nanotechnology,
424 but also to the fact that nanominerals and mineral nanoparticles are excellent natural proxies
425 to assess the behavior and potential environmental risks of their anthropogenic counterparts.
426 In this respect, many examples of the role played by mineral nanoparticles in the
427 environment are continuously appearing (see compliations and perspectives by, e.g.,
428 Hochella et al., 2008; Maurice and Hochella, 2008; Qafoku, 2010, 2011; Barnard and Guo,
429 2012; and Barrón and Torrent, 2013) at the same time that individual nanominerals are being
430 importantly scrutinized as never before, such as imogolite (Yuan and Wada, 2012),
431 ferrihydrite (e.g. Michel et al., 2007; Manceau, 2011; Eusterhues et al., 2008; Gilbert et al.,
432 2013), and schwertmannite (Fernandez-Martinez et al., 2010; French et al., 2012).
433 Waychunas and others provide particularly useful and illustrative summaries of the chemistry
434 and physics of the unique nature of mineral nanoparticles (Waychunas et al., 2005;
435 Waychunas and Zhang, 2008).

436 Crystallinity and disorder play an essential role in influencing the specific behavior of
437 nanominerals and mineral nanoparticles. It is well known that as the size of a nanoparticle is
438 decreased, a much higher percentage of the mineral structure is at or near the surface.
439 Notwithstanding, the study of the position of atoms, vacancies and defects at the surface of
440 nanoparticles and nanominerals remains elusive and mostly unexplored. Some of the most
441 advanced work at the forefront of this topic shows how mineral nanoparticles and
442 nanominerals typically exhibit structural relaxation (inducing internal disorder and strain)
443 that can vary with decreasing particle size and changes in composition (e.g., Drits and
444 Tchoubar, 1990; Lanson et al., 2002; Gilbert et al., 2004; Drits et al., 2005; Michel et al.,

2007; Michel et al., 2010; Gilbert et al., 2013; Manceau et al., 2013). Along this same line of reasoning, it has been proposed that mineral nanoparticles can undergo internal structural changes as a response to changes in the surface environment (Zhang et al., 2003). In addition, the presence of nanoscale pores (also know as "nanopipes", only 1-3 nanometers in diameter) have recently been observed in 10 to 40 nm hematite nanoparticles by means of HRTEM and 3D electron tomography based on HAADF-STEM imaging (Echigo et al., 2013). The existence of these "nanopipes" enhances mineral dissolution by extending within the nanoparticle the commonly highly reactive sites at its surface.

The studies mentioned above also suggest that atomic structure, and particularly the role of surface and near-surface atomic structure modifications, must play a role in the kinetics of reactions of interest; but importantly also in the overall thermodynamic stability fields for the phases of key interest. This idea has been around for many decades, most notably demonstrated (in principal, and in a geochemical context) in a pioneering article by Langmuir (1971). But it has not been until relatively recently that the system thermodynamics primarily for anhydrous and hydrated transition metal oxides has been quantitatively and reliably worked out (Navrotsky et al., 2008, 2010; Navrotsky, 2011). The primary importance of this work is the realization that surface enthalpy becomes a critical factor in the thermodynamic stability of polymorphs or within a family of related minerals (e.g. iron oxides) as one moves from the micron to the nanometer size regime. The upshot is that phases only metastable in larger sizes may become thermodynamically stabilized/prefered at the nanoscale. Caution is in order here, in that in real environmental systems intrinsic factors (varying defect states, chemical impurities, phase heterogeneity, etc.) and extrinsic factors (e.g. system pH, Eh, and various organic and inorganic sorbents besides, or in addition to water) will potentially all adjust thermodynamic phase stability boundaries. Yet, it is the principle and landscape of both kinetic and thermodynamic affects that are important to realize here, if not to exactly understand or measure, but to at least appreciate their influence on the overall environmental system.

Amorphous-nanocrystalline transitional phases

Definitions, categories, classifications, and structural models are convenient (and useful) human constructs, but not necessarily what nature presents to us. Nevertheless, Figure 2 attempts to incorporate the latest thinking in the progression of materials between SRO, MRO, and LRO states. We admit that even this more complex view presented in Figure 2 is an oversimplification, but hopefully it is closer to what nature presents to us compared to

previous attempts at this sort of description. The most important point here, however, is that this view necessitates critical transitional states, or phases, which in any given system may be as influential, or more influential, than phases that are considered stable and often most abundant.

An example of these transitional phases is the recent redefinition of schwertmannite, a well-known natural material classified as a mineral, and recently more specifically as a "polyphasic nanomineral" (French et al., 2012). This new term was coined to describe the existence of two different nano-domains within schwertmannite nanoparticles (Fig. 1A). Using HRTEM, it was possible to differentiate goethite-like nano-domains within a preponderant amorphous sulfate-rich matrix, the combination giving us what it is known as schwertmannite. As suggested by French et al., the physical and chemical bulk response of a polyphasic nanomineral should reflect the characteristics and predominance of the different nano-domains. By the same token, for example, the solubility of polyphasic nanominerals has to be highly affected. Concerning this issue, an alternative thermodynamic model has been recently proposed combining the polyphasic nature of schwertmannite and a progressive solubility product range to reproduce the broad solubility of this nanomineral in nature (Caraballo et al., 2013).

Another important open aspect of this type of material is to elucidate a mechanism for polyphasic nanominerals formation. Although this specific case remains unclear, some other similar cases suggest non-classical nucleation in water-based solutions (Gebauer and Cölfen, 2011) which need to be carefully considered. This is presented as an alternative option to the classical view of the crystallization process (different stages of crystallization proceeding via attachment of basic monomers like atoms, ions or molecules). This non-classical crystallization relies on polymers and the smallest nanoparticles as the primary crystal growth units. This construct effectively goes beyond, or must be considered in addition to, growth by oriented attachment of nanoparticles (Li et al, 2012, and references therein). Gebauer et al. (2008) first suggested that stable prenucleation calcium carbonate clusters are in fact the relevant species leading to the formation of different amorphous calcium carbonate phases that eventually will evolve into other crystalline calcium carbonates like calcite, vaterite, and aragonite. To date, no direct structural characterization of prenucleation clusters has been obtained, although recent studies are compiling indirect evidence for this phenomenon (Gebauer and Cölfen, 2011). Along these lines, cryogenic HRTEM and electron tomography have proven helpful in obtaining *in situ* images and 3D representations of

prenucleation clusters, as recently shown for calcium carbonates in aqueous solutions (Pouget et al., 2009) and calcium phosphate in simulated body fluids (Dey et al., 2010). However, paralleling this view is an alternative model known as liquid-liquid separation (reviewed and extended recently by Wallace et al., 2013). Supported by previous NMR, light scattering, and electron microscopy evidence, as well as spinodal decomposition theory and modeling, molecular dynamics simulations, and total x-ray pair distribution functions, Wallace et al. (2013) suggest that amorphous calcium carbonate (ACC) forms as a result of the formation of a dense liquid phase at a certain aqueous calcium carbonate ion activity product (depending on extrinsic conditions like temperature and pressure) via long-ago established spinodal decomposition principles. Coalescence and at least partial dehydration of these nanoscale clusters is suggested to result in the formation of the ACC phase.

Most recently, Lupulescu and Rimer (2014) used time-resolved atomic force microscope images under hydrothermal conditions to show that silicalite-1 (a siliceous ZSM-5 zeolite) grows in classical and non-classical pathways at the same time, by simultaneous accretion of silica molecules as the primary growth unit, but also by the aggregation of metastable silica nanoparticle precursors.

We suggest that all of these studies have vitally important developmental impact in aquatic systems where the presence of polymeric species and small clusters have previously been suggested, suspected, or confirmed. These include the prenucleation units of silicic acid polymers during the silicification process (Perry, 2003), as well as Al-Keggin polyoxocations in the origin of aluminum flocs in rivers bearing metal contaminants (Furrer et al., 2002). The incorporation of synchrotron X-ray scattering, the latest TEM methods, and a myriad of other analytic and experimental methods focused on the study of nucleation and growth of well known phases (as well as lesser known phases like polyphasic nanominerals) are expected to significantly advance the understanding of these important environmentally-relevant chemical phenomena.

Mesocrystals

Advances in crystallization pathways as discussed above, and also the developing science of nanophase oriented aggregation (Penn and Banfield, 1998; Banfield et al., 2000; Li et al., 2012), help in part to explain and visualize the formation of mesoscopically structured crystals, also referred to as mesocrystals. The highly oriented subunits forming a mesocrystal differentiate this material from polycrystals characterized by randomly oriented

543 units, whereas in both cases the identifiable nano-sized units distinguish them from single
544 crystals. Several mechanisms of formation can generate mesocrystals, but at the same time
545 they can lead to the formation of single crystals; therefore it is important to emphasize that
546 the term mesocrystal defines the structure of a material rather than its exact formation
547 mechanism. The number of mesocrystal-related studies has increased dramatically over the
548 last decade with various comprehensive review articles periodically updating several stages
549 of advances (Cölfen and Mann, 2003; Cölfen and Antonietti, 2005; Song and Cölfen, 2010).
550 Four main mechanisms generating mesocrystals have been proposed to date (Fig. 2): a)
551 alignment of nanoparticles by an oriented organic matrix, b) ordering by physical fields and
552 interparticles forces, c) mineral bridges and d) space constraints. For a detailed discussion of
553 the different mechanisms and specific cases, the reader is referred to Song and Cölfen (2010).

554 The specific case of oriented aggregation will be discussed here to illustrate once
555 again the impressive advances in the understanding of mineral crystallinity as a result of
556 technological progress. Oriented aggregation is a non-classical crystal growth mechanism
557 that involves the self-assembly of primary nanocrystals, including crystallographic
558 reorganization within the self-assemblies and conversion to oriented aggregates (Yuwono et
559 al., 2010). The use of HRTEM has allowed for the direct observation of this non-classical
560 crystallization mechanism for natural iron oxyhydroxides biomineralization products
561 (Banfield et al., 2000). The next step in the understanding of this process was made possible
562 by the application of cryogenic HRTEM (Yuwono et al., 2010). This technique enables direct
563 observation of nanoparticles in aqueous suspension thanks to the preservation of the three-
564 dimensional arrangement of nanoparticles as a result of water vitrification. However, more
565 recently the actual observation of the aggregation, attachment and growth of ferrihydrite
566 nanoparticles was finally achieved directly in aqueous solution and in real-time using
567 HRTEM and a water-filled TEM environmental cell (Li et al., 2012). It was observed how, at
568 the time of attachment, ferrihydrite nanoparticles shared the same crystallographic
569 orientation with their neighbors (either exact structural alignment or twin-related), and how
570 after the attachment event, atoms filled the interface region on a time scale on the order of 10
571 to 100 s. This study also observed attachment and recrystallization of misaligned particles
572 and dissolution of small particles in the vicinity of larger ones; showing that, even in systems
573 where oriented attachment is dominant, classical crystallization process like Ostwald
574 ripening can play an important role.

Another example of how the synergetic use of several techniques (HRTEM, NMR, FTIR and synchrotron XRD) is leading to a unique level of detail in the understanding of mineral crystallinity is shown in a recent study of the structure-property relationships of biological mesocrystals in the adult sea urchin spine (Seto et al., 2012). This study has shown how each spine comprises a highly oriented array of Mg-calcite nanocrystals in which amorphous regions and organic macromolecules are embedded. This case illustrates how complex hierarchical structures can diffract as a single crystal and yet fracture as a glassy material.

IMPLICATIONS

Our experience in looking at the environmental impacts of mining (Hochella et al., 1999, 2005a, 2005b, 2008; Plathe et al., 2010, 2013; French et al., 2012; Mantha et al., 2012; Schindler et al., 2012) have shown us repeatedly that whenever we look at the inorganic portion of environmental samples in detail with TEM, we invariably find 1) minerals that are known but that have not previously been reported in that environment; 2) minerals that show a wide range of crystallinity, some of which have never been described before; and 3) amorphous materials that have not been described before, and with compositions that range from simple to complex. Because these phases are minute, and/or often not highly crystalline, and/or less abundant, they are typically ignored or more likely missed altogether. Yet they can be (and most often are) highly relevant to important aspects of how the (bio)geochemistry of that system works, or how the system evolves with time, or how that system impacts the ecosystem in which it exists, as well as how they impact surrounding ecosystems. For example, in metal-contaminated mine-drainage systems that can extend tens to hundreds of kilometers, nanominerals and mineral nanoparticles can be highly reactive toxic metal sorbents, and in the case of very small nanoparticles, they can be hyper-reactive (O'Reilly and Hochella, 2003; Madden and Hochella, 2005; Hochella et al., 2005a; French et al., 2012; Caraballo et al., 2013). It has been shown that a hyper-reactive nanophase at just 1% concentration can completely dominate a critical geochemical reaction in such a system (Fig. 1.2 in Hochella et al., 2012).

Independently, other groups have been able to also overcome many of the distinct challenges of sorting out the identification and assessment of key naturally-occurring nanomaterials in highly complex environmentally-relevant water systems. They have done so in a variety of ways, including: imaging and analytic techniques centered around synchrotron

607 x-ray methods and TEM's (as described in this paper), sophisticated filtering methods
608 (tangential and flow field fractional methods), column experiments with natural samples,
609 molecular biology assessments, sequential extraction, electrophoretic mobility methods, ICP-
610 MS, NMR, Mossbauer spectroscopy, and so on. Key publications include Bertsch and
611 Seaman (1999), Lead and Wilkinson (2006), Moreau et al. (2007), Theng and Yuan (2008),
612 and Weber et al. (2009). The overarching theme of these papers, and some of the papers that
613 they cite, is similar to ours, showing great and often unexpected mineral/biological
614 complexity within natural soil, sediment, aquifer, and surface water systems at the nanometer
615 to micron scale. Controlling influences of key (bio)geochemical reactions of interest (e.g.
616 contaminant association and transport) often have not been predicted or even identified by
617 idealized laboratory-based experiments or observations using a single or a few system
618 components under idealized conditions. Even the most common or obvious minerals or
619 organic/biological agents observed in the field are often not a controlling influence in the
620 most interesting/important overall chemistry that is attempting to be understood. Further still,
621 sub-nanometer science has even taken some interesting and unexpected turns. Fourier
622 transform mass spectrometry and voltammetric analysis has been used to find, characterize,
623 and sort out the importance of multinuclear clusters (e.g. M_3S_3 or M_4S_6), which are sub-
624 nanometer in size (e.g. Rozan et al., 2000; Luther and Rickard, 2005). These clusters are
625 what might be considered the very smallest of the nanoparticles with their own remarkable
626 behaviors and environmental significance.

627 As all of the above studies have shown, non-crystalline and poorly crystalline
628 materials, as well as nanomaterials in all degrees of crystallization, are typically much more
629 difficult to find and to study in environmental samples that are invariably complex and very
630 difficult with which to deal. Overall, this has resulted in a distinct under-representation of the
631 studies that look at natural systems relative to the overall scientific production output within
632 this field.

633 The technological revolution described herein is enabling the direct study of minerals
634 and their formation in their natural environmental compartments, generating a more realistic
635 understanding of their response to changes in the physical chemistry of the environmental
636 system and vice versa. The next several years are also expected to experience a notable
637 proliferation in the number of synchrotron, FEL and HRTEM "real time" studies intended to
638 reveal non-classical crystallization pathways. These studies, among other things, should be

able to unravel the role of polymers and prenucleation clusters in the early stages of mineral formation.

Mineral thermodynamics, reaction kinetics, and solubility are other research areas where a deep influence of future discoveries in mineral crystallinity can be anticipated. To this end, it is compelling to obtain a better understanding of nanomineral and mineral nanoparticle singular characteristics, such as crystal structure, surface disorder, nano-domains, nano-porous heterogeneity, and 3D morphologies.

The varied, unique, and/or sometimes highly complex characteristics of mesocrystals (e.g., high crystallinity and porosity, nanocrystalline individual subunits or organic-inorganic hybrid structures) enhance their functionality (including in living systems) compared to their single crystal counterparts. The discovery of new naturally occurring mesocrystals, as well as a deeper understanding of their formation mechanisms, will allow us to transfer their special properties to new synthetic and biomimetic materials.

The forthcoming discoveries in mineral crystallinity within complex environmental systems will have a significant effect on the understanding of the roles played in nature by amorphous and nano-sized neoformed mineral phases, mineral nanoparticles, and mesocrystals. In addition, this will have an important impact in other areas like material sciences and nanotechnology where natural materials and processes will likely inspire new synthetic materials and nanotechnological applications.

ACKNOWLEDGMENTS

M.A.C. was financially supported by the Spanish Ministry of Education and the Post-doctoral International Mobility Sub-programme I+D+i 2008-2011. Grants from the U.S. Department of Energy (DE-FG02-06ER15786) and the Institute for Critical Technology and Applied Sciences at Virginia Tech also provided financial support for this project. We are also appreciative of the support from the National Science Foundation (NSF) and the Environmental Protection Agency through the Center for Environmental Implications of NanoTechnology (CEINT) funded under NSF Cooperative Agreement EF-0830093. We would also like to thank four anonymous reviewers and especially Dr. Alejandro Fernández-Martinez (Associate Editor) for their many and thoughtful comments that significantly improved the quality of this paper.

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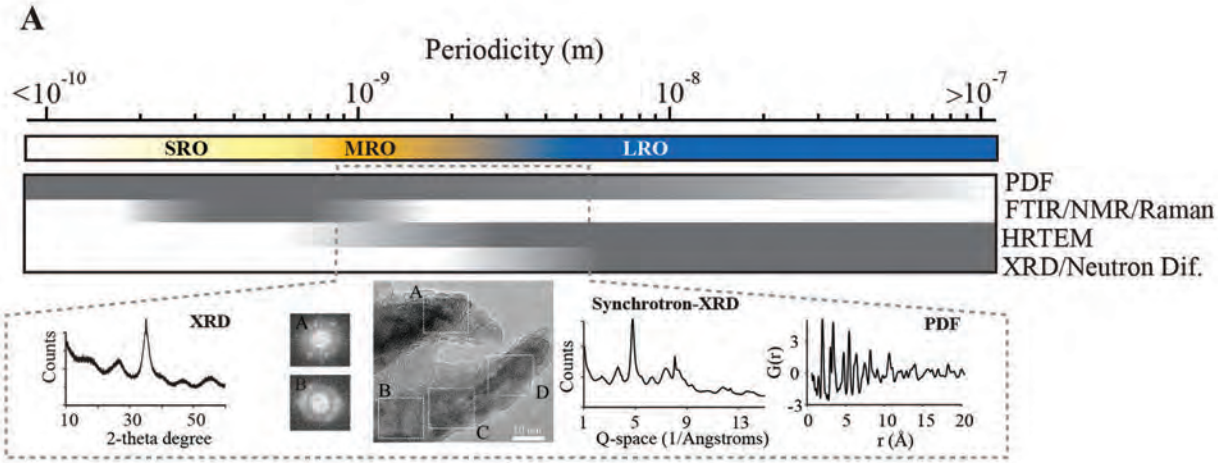
FIGURE CAPTIONS

FIGURE 1A) Resolution limits of some common techniques used in the measurement of mineral crystallinity. The progressive fading from grey to white marks the lost of resolution of the different analytical techniques in the figure. The need of a multi-technique characterization to properly understand complex mineral phases is shown in the dashed extended area by the use of schwertmannite as a proxy for polyphasic nanominerals. B) Peak brilliance comparison between a selection of state-of–the-art 3rd generation synchrotrons and free electron lasers (FEL). Abbreviations: Advanced Light Source (ALS), Berliner Synchrotron (BESSY), Advance Photon Source (APS), European Synchrotron Radiation Facility (ESRF), Positron Electron Ring Angle (PETRA III), UE65 is part of PETRA, Super Photon Ring 8GeV (Spring-8), Free Electron Laser at Hamburg (FLASH), LINAC Coherent Light Source (LCLS), European XFEL operational in 2015 (XFEL). C) Evolution of Transmission Electron Microscopy (TEM) resolution. The graphic within the extended dashed area corresponds to the resolutions as a function of electron energy recently achieved by TEAM 0.5 project. Abbreviations: high vacuum (HV), high resolution (HR).

996

997 FIGURE 2. Schematic categorization of the natural progressive transition between
998 amorphous and crystalline materials. The most relevant emerging areas within mineral
999 crystallinity in environmental systems discussed in the main text have been exemplified with
1000 some specific cases. The four categories shown within the mesocrystals inset correspond to
1001 the alignment of nanoparticles by: a) organic matrices, b) physical fields and interparticles
1002 forces, c) mineral bridges and d) space constrains.

Fig. 1


A
Periodicity (m)
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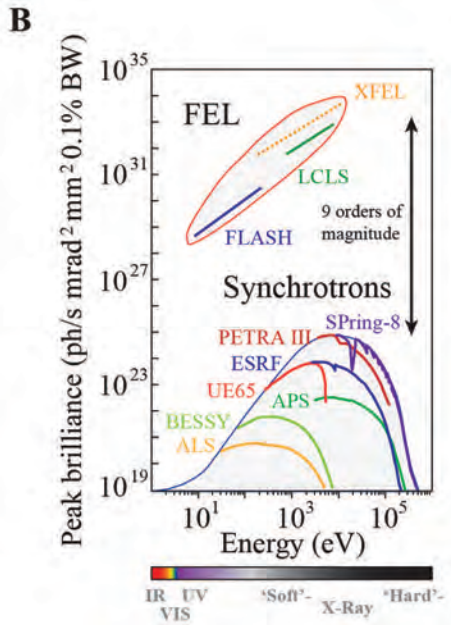
10-9
10-8
>10-7
SRO
MRO
LRO
PDF
FTIR/NMR/Raman
HRTEM
XRD/Neutron Dif.
XRD
Counts
2-theta degree
Synchrotron-XRD
Q-space (1/Angstroms)
PDF
G(r)
r (Å)


B
Peak brilliance (ph/s mrad2 mm2 0.1% BW)
FEL
XFEL
LCLS
FLASH
9 orders of magnitude
Synchrotrons
SPring-8
PETRA III
ESRF
UE65
APS
BESSY
ALS
Energy (eV)
IR UV VIS
'Soft'-X-Ray
'Hard'-

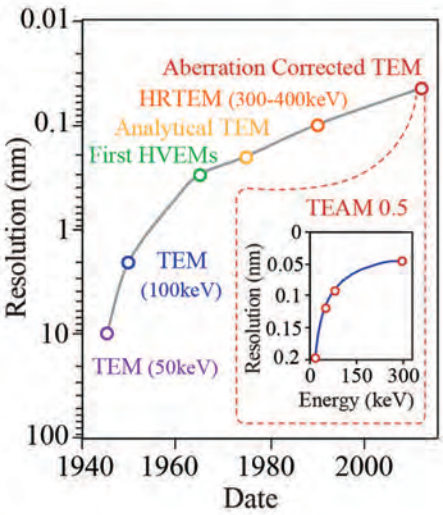
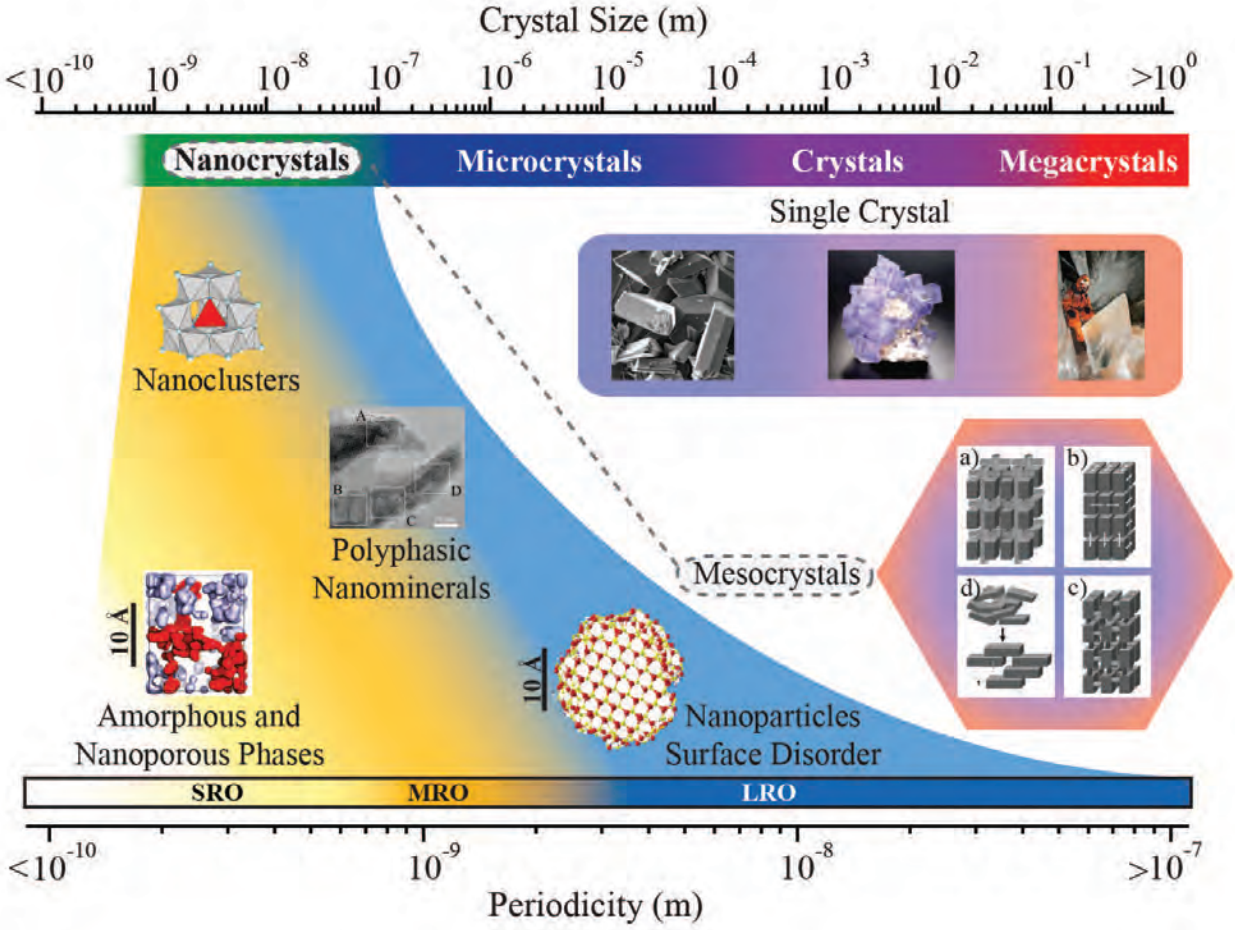

C
Resolution (nm)
Aberration Corrected TEM
HRTEM (300-400keV)
Analytical TEM
First HVEMs
TEAM 0.5
TEM (100keV)
TEM (50keV)
Energy (keV)
Date

Fig. 2


Crystal Size (m)
<10^-10
10^-9
10^-8
10^-7
10^-6
10^-5
10^-4
10^-3
10^-2
10^-1
>10^0
Nanocrystals
Microcrystals
Crystals
Megacrystals
Single Crystal
Nanoclusters
A
B
C
D
Polyphasic
Nanominerals
Mesocrystals
a)
b)
c)
d)
10 Å
Amorphous and
Nanoporous Phases
10 Å
Nanoparticles
Surface Disorder
SRO
MRO
LRO
<10^-10
10^-9
10^-8
>10^-7
Periodicity (m)